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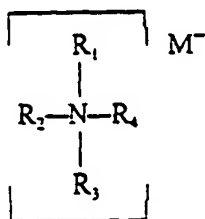
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(54) **Organoclay compositions manufactured with organic acid ester-derived quaternary ammonium compounds, their preparation and non-aqueous fluid systems containing such compositions**

(57) An organophilic clay comprising the reaction product of:

- (a) a smectite-type clay; and  
(b) a quaternary ammonium compound or compounds selected from the group consisting of:



wherein  $R_1$  is an alkyl or aralkyl- ester group having 8 to 30 carbon atoms and  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from the group consisting of (i)  $R_1$ , (ii) long chain linear or branched alkyl (including methyl), aliphatic or aromatic groups having 1 to 30 carbon atoms (such groups can also include hydroxylated groups); (iii) aralkyl groups, which are benzyl and substituted benzyl moieties, including such groups having fused ring moieties having linear chains or branches of 1 to 30 carbon atoms; (iv) aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents; (v) beta, gamma unsaturated groups having six or less carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (vi) hydrogen and  $M^-$  is an anion selected from the group consisting of chloride, methylsulfate, acetate, iodide and bromide.

The organophilic clay is used in a non-aqueous fluid system such as paints, inks, and coatings to provide rheological properties.

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the organoclay is made in part from organic acid-derived esters. These organoclays show in a number of circumstances either increased efficiency or substantially equivalent performance versus conventional prior art organoclays, and they can be made with quaternary compounds of either present, or anticipated, lower cost. These novel organoclays have a different structure with increased x-ray diffraction pattern  $d_{001}$  spacings. The manufacture of these organophilic clays eliminate the need to use nitrile quaternaries of the type which European environmental authorities have found to be environmentally unfriendly. The present invention provides an improved, more biodegradable organophilic clay for gelling or thickening non-aqueous organic and solvent-based compositions.

Thus, according to one aspect of the invention, an organophilic clay is provided which comprises the reaction product of:

- (a) a smectite-type clay having a cation exchange capacity of at least about 75 milliequivalents per 100 grams of clay, 100% active clay basis;
- (b) one or more organic cations in an amount sufficient to satisfy at least about 75% of the cation exchange capacity of the smectite-type clay, and of any optional organic anion(s), wherein the cation or cations are quaternary ammonium compound(s) derived from organic acid-derived esters; and optionally
- (c) one or more organic anion(s) that are capable of reacting with the organic cation(s) to form an organic cation/organic anion ion pair complex which is intercalated with the clay.

The present invention also contemplates a process for preparing an organophilic clay which comprises:

- (a) preparing an aqueous slurry of a smectite-type clay having a cation exchange capacity of at least about 75 milliequivalents per 100 grams of clay, 100% active clay basis;
- (b) heating the slurry to a temperature of from about 20°C to 100°C;
- (c) adding to the slurry:
  - (i) one or more organic cation(s) which are quaternary ammonium compounds derived from organic acid-derived esters; and optionally
  - (ii) one or more organic anion(s) that are capable of reacting with the organic cation(s) to form an organic cation/organic anion pair which is intercalated with the clay;
- (d) reacting the resulting mixture for a sufficient time to form an organophilic clay; and
- (e) recovering the organophilic clay.

The invention also provides non-aqueous organic compositions thickened with the above-indicated organophilic clay. A third aspect of the invention therefore relates to a non-aqueous fluid system which comprises:

- (a) a non-aqueous composition; and
- (b) an organophilic clay comprising the reaction product of:

- (i) a smectite-type clay having a cation exchange capacity of at least about 75 milliequivalents per 100 grams of clay, 100% active clay basis;
- (ii) one or more organic cation(s) in an amount sufficient to satisfy at least about 75% of the cation exchange capacity of the smectite-type clay and of any optional organic anion(s), which are quaternary ammonium compounds derived from organic acid-derived esters; and optionally
- (iii) one or more organic anions that are capable of reacting with the clay and/or the organic cation(s) to form the above described complex.

#### Description of the Preferred Embodiments:

As stated above, one aspect of the present invention relates to improved, more efficient organophilic clays. These organophilic clays are prepared by reacting a smectite-type clay with an organic cation or cations provided by specific quaternary ammonium compounds.

The clays used to prepare the organophilic clay of this invention are cation-exchangeable smectite clays which have a cation exchange capacity of about 75 or greater milliequivalents per 100 grams of clay, 100 percent active basis (i.e. beneficiated and essentially free of non-clay impurities). Smectite-type clays are well known in science, geology and in the art of rheological additives, and are commercially available from a variety of sources both in the United States and throughout the world. They are unique among clays in that they exhibit the phenomena of swelling to many

examples are 1) bentonite, and 2) hectorite.

Cation-exchangeable clays can also be synthesized usually from a montmorillonite base clay, so as to possess certain chemical and physical characteristics in order to make such clays valuable in the practice of the present invention.

The above-described clays, especially the bentonite-type clays, are preferably converted to the sodium form if they are not already in this form. Commercially important representatives of such smectite clays used to make the organoclays of this invention are sodium and calcium bentonite and hectorite. The cation exchange capacity of these smectite-type clays can be determined by the well-known methylene blue method or the ammonium acetate method. Smectite-type clays prepared synthetically by either a pneumatolytic or, preferably, a hydrothermal synthesis process may also be used to prepare the novel products of this invention.

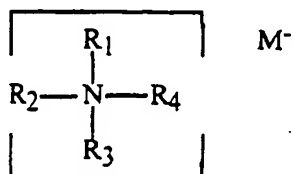
The most preferred clays used in the present invention are Wyoming bentonite, particularly sodium bentonite, and hectorite from Hector, California in the Mojave Desert. Bentonite and hectorite clays have high bonding power and react easily with the specific organic quaternary compounds described hereafter.

In addition, it will be understood that the above listed smectite-type clays which have been subjected to the application of shear may also be used to make the organoclays of the instant invention. To achieve shearing of the smectite-type clay, the clay is typically dispersed in water at a concentration of from about 0.5 to about 30% by weight. The slurry may optionally be first centrifuged to remove non-clay impurities which constitute about 10% to about 50% of the starting clay composition. Of course, if in some cases the clay has previously been treated, such as by the clay vendor, to remove such impurities, the clay as purchased without centrifuging can be formed into a slurry and subjected to shear conditions.

Shear can be imparted to the smectite-type clay slurry by means of commercially available equipment that is known to impart high shear to the material. Illustrative of such equipment are a Manton-Gaulin Homogenizer available from the APV Gaulin Company, a Tekmar SD-45 Homogenizer, a Sharples Super Centrifuge available from Sharples Division of Pennwalt Corporation, an Oakes mill available from Oakes Machinery, a Microfluidizer available from Microfluidics, a division of Biotechnology Corporation, and similar devices which can impart high laminar and turbulent shear to the clay slurry. Exemplary conditions using a Manton-Gaulin homogenizer are a pressure in the range from about 500 to about 8,000 psi with one or more passes of the clay slurry through the homogenizer. Representative processes for shearing clay slurries are described in U.S. Patent No. 4,743,098 which is herein incorporated by reference.

The organic cations which are useful in this invention may be selected from a variety of nitrogen-based quaternary materials that are capable of exchanging cations with the selected smectite-type clay. The organic cations which are reacted with smectite type clay to prepare the inventive organophilic clays have a positive charge localized on a single nitrogen atom within the compound.

For this invention, the organic cation is provided by specific quaternary ammonium compounds derived in whole or in part from organic acid - derived esters. This organic cation is provided by a quaternary ammonium compound selected from the group consisting of the following formulae:



wherein  $R_1$  is an alkyl or aralkyl-ester group having 8 to 30 carbon atoms as described below and  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from the group consisting of (i)  $R_1$ , (ii) long chain linear or branched alkyl (including methyl), aliphatic or aromatic groups having 1 to 30 carbon atoms (such groups can also include hydroxylated groups); (iii) aralkyl groups, such as benzyl and substituted benzyl moieties, including such groups having fused ring moieties having linear chains or branches of 1 to 30 carbon atoms; (iv) aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents; (v) beta, gamma unsaturated groups having up to six carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (vi) hydrogen.  $M^-$  is an anion, typically chlorido, methyl sulfato, acetate, iodide or bromide.

This quaternary ammonium compound must contain at least one linear or branched, saturated or unsaturated alkyl or aralkyl-ester  $R_1$  group having 8 to 30 carbon atoms. Such ester groups are of the general formula:

anthracene, and phenanthrene.

Beta, gamma unsaturated alkyl groups which may be included in organic cation component of the organophilic clay gellants of the invention may be selected from a wide range of materials well known in the art. These compounds may be cyclic or acyclic, unsubstituted or substituted with aliphatic radicals containing up to 3 carbon atoms such that the total number of aliphatic carbons on the beta, gamma unsaturated radical is 6 or less. The beta, gamma unsaturated alkyl radical may be substituted with an aromatic ring that likewise is conjugated with the unsaturated beta, gamma moiety or the beta, gamma radical may be substituted with both aliphatic radicals and aromatic rings.

A representative examples of beta, gamma unsaturated alkyl groups include 2-cyclohexenyl. Representative examples of acyclic beta, gamma unsaturated alkyl groups containing 6 or less carbon atoms include propargyl; allyl (2-propenyl); crotyl (2-butenyl); 2-pentenyl; 2-hexenyl; 3-methyl-2-butenyl; 3-methyl-2-pentenyl; 2,3-dimethyl-2-butenyl; 1,1-dimethyl-2-propenyl; 1,2-dimethyl propenyl; 2,4-pentadienyl; and 2,4-hexadienyl. Representative examples of acyclic-aromatic substituted compounds include cinnamyl(3-phenyl-2 propenyl); 2-phenyl-2-propenyl; and 3-(4-methoxyphenyl)-2-propenyl. Representative examples of aromatic and aliphatic substituted materials include 3-phenyl-2-cyclohexenyl; 3-phenyl-2-cyclopentenyl; 1,1-dimethyl-3-phenylpropenyl; 1,1,2-trimethyl-3-phenyl-2-propenyl; 2,3-dimethyl-3-phenyl-2-propenyl; 3,3-dimethyl-2-phenyl-2-propenyl; and 3-phenyl-2-butenyl.

Hydroxyalkyl groups may be selected from a hydroxyl substituted aliphatic radical wherein the hydroxyl is not substituted at the carbon atom adjacent to the positively charged atom; the group has from 2 to 6 aliphatic carbon atoms. The alkyl group may be substituted with an aromatic ring independently from the 2 to 6 aliphatic carbons. Representative examples include 2-hydroxyethyl; 3-hydroxypropyl; 4-hydroxypentyl; 6-hydroxyhexyl; 2-hydroxypropyl; 2-hydroxybutyl; 2-hydroxypentyl; 2-hydroxyhexyl; 2-hydroxycyclohexyl; 3-hydroxycyclohexyl; 4-hydroxycyclohexyl; 2-hydroxycyclopentyl; 3-hydroxycyclopentyl; 2-methyl-2-hydroxypropyl; 1,1,2-trimethyl-2-hydroxypropyl; 2-phenyl-2-hydroxyethyl; 3-methyl-2-hydroxybutyl; and 5-hydroxy-2-pentenyl.

The groups found to be most effective in producing the organic ester-derived quaternary ammonium compounds of the type found useful in this invention, in addition to one or more  $R_1$  organic acid - derived ester groups of the type described are, (a) one or more methyl groups, (b) one or more benzyl groups, (c) one or more long chain alkyl groups, and combinations thereof. Most preferred  $R_1$  groups are those derived from coconut oil. Specific quaternaries found most useful are dicoco esters of dimethyl diethanol ammonium chloride.

A broad variety of quaternary ammonium compounds are disclosed in U.S. Patent No. 4,141,841 issued to Proctor & Gamble Company - see also U.S. Patent No. 3,862,058 also issued to Proctor & Gamble.

The preparation of quaternary compounds used to make organophilic clays of this invention can be achieved by techniques well-known in the art. For example, when preparing a quaternary ammonium compound of the type described, one skilled in the art may begin with a readily available tertiary alkanolamine, such as triethanolamine, methyl or ethyl diethanolamine, dimethyl or diethyl ethanolamine, methyl or ethyl dipropanolamine, or dimethyl or diethyl propanolamine, which may be reacted with one or more fatty acids under esterification reaction conditions; the practitioner will recognize that the molar ratio of fatty acid that react with the hydroxyl moieties of the alkanol amine preferably should be at most 1:1, and can be less than 1:1. When the ratio is less than 1:1, then the resulting ester groups will be statistically distributed among the alkanol groups. If, on the other hand, the ratio of fatty acid to alkanol moieties is greater than 1:1, some amount of the fatty acid will remain unesterified following the esterification reaction, which amount may or may not have some small adverse effect on subsequent reactions of the product of this reaction.

Following the esterification of some of all of the hydroxyl moieties of the alkanol groups of the tertiary amine, the reaction product may, optionally, be reduced with a diluent, typically water and/or a low molecular weight alcohol such as methanol, ethanol, 2-propanol or butanol, and reacted with an alkylating agent under conditions well known to one skilled in the art to form the quaternary ammonium compounds useful in making the organoclays of this invention.

The organic anion(s) optionally employed in the products of the invention may be selected from a wide range of materials that are capable of reacting with the organic cations in order to form an organic cation/organic anion complex. The molecular weight of the organic anion is preferably 3,000 or less, and more preferably 1,000 or less, and contains at least one anionic moiety per molecule so as to permit the formation of the organic cation/organic anion complex which then becomes intercalated between the clay platelets.

Preferred organic anions are derived from carboxylic acids, such as stearic acid, oleic acid, palmitic acid, succinic acid, tartaric acid, etc.; sulfonic acids; and alkyl sulfates, such as the lauryl half ester of sulfuric acid and mixtures thereof.

The organic anion, which may include mixtures of organic anions, is reacted with the organic cation and smectite-type clay to form the desired organophilic clay gellant. The organic anion may be added to the reaction mixture in acid or salt form. Exemplary of the latter form are alkali metal salts, alkaline earth salts, ammonium and organic amines.

Representative salts of the organic anion are those formed with hydrogen, lithium, sodium, potassium, magnesium, calcium, barium, ammonium and organic amines such as ethanolamine, diethanolamine, triethanolamine, methyldiethanolamine, butyldiethanolamine, diethylamine, dimethylamine, triethylamine, dibutylamine, and so forth, and mixtures thereof. The most preferred salt form is with sodium.

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The organophilic clay complexes of the invention are added to the non-aqueous compositions in amounts sufficient to obtain the desired rheological properties. Amounts of the organophilic clay complexes in the non-aqueous compositions are from about 0.01% to 15%, preferably from about 0.3% to 5%, based on the total weight of the non-aqueous fluid system.

The following examples are given to illustrate the invention, but are not deemed to be limiting thereof. All percentages given throughout the specification are based upon weight unless otherwise indicated.

### EXAMPLE 1

This example and Examples 2 to 6 illustrates the preparation of organoclays according to the present invention.

In this example, 45.00 grams of beneficiated un-sheared Wyoming bentonite clay slurry was diluted with water to form a 2% by weight dilute slurry of bentonite in water. The slurry was heated to 65°C in a reaction flask equipped with a stirrer, thermometer and addition funnel. 28.54 grams of a dicoco ester of dimethyl diethanol ammonium methylsulphate quaternary compound, commercially available as TETRANYL ACHF-2 from Kao Corporation, was added to the clay slurry. The mixture was stirred for 30 minutes at 65°C. The product was filtered through a Buchner funnel to collect the solids. The wet solids were reslurried in 1500 grams of water at 65°C for 20 minutes and then recollected on a Buchner funnel. The organoclay "filtercake" was dried at 45°C for 16 hours.

### EXAMPLE 2

The procedure of Example 1 was repeated, except that 34.62 grams dihydrogenated tallow ester of dimethyl diethanol ammonium methylsulphate, commercially available as TETRANYL AHT-2 from Kao Corporation was used.

### COMPARATIVE EXAMPLE A

For comparative purposes, the procedure of Example 1 was repeated, except that 24.15 grams of dimethyl dihydrogenated tallow ammonium chloride, a quaternary compound commonly used to make a variety of commercial organoclays, was added.

### EXAMPLES 3-6

The compositions were prepared according to the procedure of Example 1, except that 28.54 grams of the following quaternary ammonium compounds were used:

- Example 3 - dihydrogenated tallow ester of dimethyl diethanol ammonium chloride
- Example 4 - dihydrogenated tallow ester of methyl triethanol ammonium methylsulphate
- Example 5 - dicoco ester of methyl triethanol ammonium methylsulphate
- Example 6 - dicoco ester of dimethyl diethanol ammonium chloride

### EXAMPLES 7-19

A typical organic system paint formulation was prepared according to Formulation 1.

#### Formulation 1

Long Oil Alkyd Paint

Ingredients	Description	Manufacturer	Amount (Pounds)
Millbase			
Beckosol 10-060	Long oil alkyd	Reichhold	105.76
Mineral Spirits 66/3	Solvent		70.60
Organoclay			7.17
MeOH/H <sub>2</sub> O 95/5	Polar activator		2.39
KRONOS 2101	Titanium Dioxide	KRONOS	325.00

The invention thus being described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the claims.

## Claims

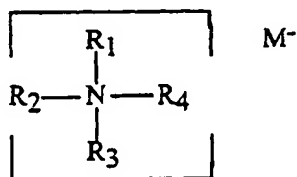
1. An organophilic clay for providing rheological properties to non-aqueous fluid systems comprising the reaction product of:

- (a) one or more smectite-type clays having a cation exchange capacity of at least about 75 milliequivalents per 100 grams of clay, 100% clay, active clay basis; and
- (b) one or more quaternary ammonium compounds derived from an organic acid-derived ester in an amount sufficient to satisfy at least about 75% of the cation exchange capacity of the smectite-type clay.

2. The organophilic clay of claim 1, wherein one or more organic anions are included in the reaction product to form a complex, the quaternary ammonium compound(s) being present in amount sufficient to satisfy at least about 75% of the cation exchange capacity of the smectite-type clay and of the organic anion, and said organic anion (s) preferably being derived from carboxylic acids, sulfonic acids, alkyl sulfates or mixtures thereof.

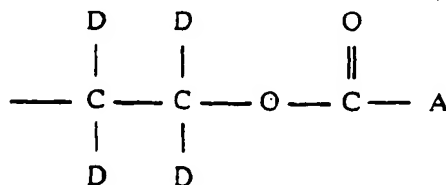
3. The organophilic clay of claim 1 or 2, wherein said smectite-type clay is selected from bentonite, hectorite and mixtures thereof.

4. The organophilic clay of any of claims 1 to 3, wherein one or more of the quaternary ammonium compounds have the formula:



wherein  $R_1$  is an alkyl or aralkyl-ester group having 8 to 30 carbon atoms and  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from (i)  $R_1$ , (ii) long chain linear or branched alkyl (including methyl), aliphatic or aromatic groups having 1 to 30 carbon atoms optionally substituted by hydroxylated groups; (iii) aralkyl groups such as benzyl and substituted benzyl moieties, including such groups having fused ring moieties having linear chains or branches of 1 to 30 carbon atoms; (iv) aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents; (v) beta, gamma unsaturated groups having up to six carbon atoms or hydroxyalkyl groups having 2 to 6 carbon atoms; and (vi) hydrogen; and  $M^-$  is an anion selected from chloride, methyl sulfate, acetate, iodide and bromide.

5. The organophilic clay of claim 4 wherein the or each  $R_1$  group has the formula:



wherein each D is independently selected from H,  $CH_3$  and  $C_2H_5$  and A is an alkyl or aralkyl radical group which group has been derived from naturally occurring oils selected from coconut oil, soybean oil and tallow.



European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 65 0004

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 204 240 A (HOECHST AG) * claims 1,3,4,6 *	1,3	C01B33/44 C09D5/04
X	* page 5, line 31 - page 6, line 7 *	8	C09D9/00
X	* page 6, line 24 - line 28; claim 8 *	9-11	C09K7/02 C10M113/16
X	DE 34 34 983 A (HOECHST AG) * claim 1 *	1,3	C09D11/00 C08K3/34
	* page 6, line 5 - line 7 *		C09D5/34
	* page 7, line 1 - line 4 *		C09J11/04
	* page 7, line 17 - line 20 *		C09K3/10
X	* page 8, line 11 - line 23 *	8	A61K7/00
X	* page 9, line 1 - line 4; claim 3 *	9-11	C11D3/12
A	DE 38 06 548 A (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) * page 9, line 33 - line 39 *		
A	LU 83 759 A (NL INDUSTRIES, INC.) * claims 1,9 *	2	
	* page 11, line 12 - page 12, line 16 *		
A	* claim 12 *	8	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D,A	& US 4 434 075 A		C01B
A	GB 2 090 584 A (NL INDUSTRIES, INC.) * claims 1,7,10 *	2	
	* page 3, line 22 - line 50 *		
A	* claims 11,19,20 *	8	
D,A	& US 4 412 018 A		
A	EP 0 542 266 A (RHEOX INTERNATIONAL, INC.) * claim 1 *		
D,A	& US 5 336 647 A		
A	GB 2 017 072 A (NL INDUSTRIES, INC.) * claim 1 *		
D,A	& US 4 208 218 A		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 May 1997	Examiner Brebion, J
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : terminological background  (I) : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			